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超伝導における遷移温度と原子間距離

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小生高エネルギー物理研究者で物性物理には素人ですが、研究の必要のため液体^{3}Heターゲットを設計製作をしました。　この時に液体ヘリウムのレベル測定に超伝導物質を使用することを考え、超伝導物質を調べる途中に、超伝導物質（元素物質）の遷移温度（Tc）と原子間距離（a）の関係を調べると、あたかも遷移温度が原子の電子雲の重なりに比例する現象がみられた。また最近の高温超伝導物質の超伝導現象を担うとみなされているCu-O層について、CuとOの距離と遷移温度の関係は元素物質と同じ関係を示す。微視的には原子・分子の周囲の量子軌道を回る電子は抵抗がなく、この量子軌道が隣同志コヒーレントに結合すれば巨視的に超伝導現象を起こすと考えられないか。以上の現象を踏まえてレポートにまとめてみました、物性研究者の方々の意見を聞きたいと思い投稿しました。

本文の要約

1）遷移温度(Tc)と原子間距離(a)の関係

$$Tc = 310 \exp(-a R_0 / (2\nu +1)) \quad K$$

$$(\nu = 0, 1, 2, \ldots\ldots \quad R_0 ; \text{常数}),$$

となり超伝導の最大遷移温度は310 Kと予想される。

2）合金超伝導では元素が異なるため単純な関係は得られないが、上式の合成で説明できるのではないか、しかし常伝導物質に比較して超伝導物質には本文図2に示すように或電子軌道の所に物質が集中してることがわかる。

3）高温超伝導物質が発見されて以来、まだBCS理論に代わり全超伝導現象を説明できる理論がないと聞いていますが、（1）と（2）の現象は、あたかもコヒーレンス長の単位で原子の電子軌道がコヒーレントに重なり電子はその量子軌道の条件を満たして抵抗なくに動くことができ、巨視的に超伝導現象をおこすと考えられる。
高温超伝導物質はCuとOの原子間距離が短く電子軌道の重なりによる電子雲の密度が高く高温に於いてもコヒーレント結合が崩れ難く高温度まで超伝導状態を保つことが出来る。

Correlation between the superconducting critical temperature and the atomic distance

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The relation between the critical temperature and atomic distance for various superconductors are studies. It is found that these described by some descrete functions, where the parameter is correlated to the atomic electron orbit of the superconductors. From those emperical functions, an upper limit of the critical temperature is estimated at 310 K for any superconductor.

In this paper the relation between the critical temperature (T_c) of the superconductive material and its atomic distance (**a**) has been systematically studied, where the atomic distance is defined as the lattice constant a of a crystal.

Recently a number of high-temperature superconducting CuO-compounds have been discovered [1]. Including these data, an extensive study was done for varous superconductive compounds and elements. According to the theory of Bardeen, Cooper and Schrieffer [2], T_c is connected exponentially to the density of states on the Fermi surface and to the interaction parameter associated with electrons lying close to the surface. In the present analysis, the exponential function is rearranged by using the atomic distance as a variable.

There have been found many superconducting materials; the pure elements (Al, Pb, ets.), the compounds (NbN, Ti_3Sb, etc.),

layered oxide compounds (YBaCuO, T1BaCaCuO, etc.) and the organic compound. We first discuss the data first for pure element materials [3]. The plot of the measured critical temperature T_c versus the atomic distance **a** for various elements is given in Fig.1. Table I shows data for the following elements ; Al, β-La, Ir, Pb, α-Th, V, Nb, Mo, Ta, Ti, Zn, Zr, Tc, Ru, Cd, Hf, Lu, Re, Os, Tl, α-La, In, α-Hg, Ga, α-U and β-Hg. If we fit these data with an exponential function, different parameters would be necessary for each group of data. We tried to fit the data with $T_c = T_0 \exp(-aR_0/(2\nu+1))$, $\nu = 0, 1, 2, 3, \ldots$, where T_0 and R_0 are the parameters to be determined for the data. The parameter are obtained as $T_0 = 310$ K, $R_0 = 6.87$ $Å^{-1}$ and 5.53 $Å^{-1}$ with fitting of these experimental data. There are two groups for the R_0 values. Those group are possibly corresponding to the electron and the hole carrier superconductors and the parameter ν could be related to the orbital anglar momentum quantum number. This form represents the overlap integration function of valenced electron in the chemical bond. According to the discrete phenomena, it is conjectured that many atomic electron orbits are combined coherently in the low temperature. Then electron pair can pass through without resistance in the coherently combined atomic electron orbit. From Fermi energy E_F, the coherent length could be estimated as $hc/E_F = 10^{-6}$ m. From the relation, also we can deduce another important result, which is the upper limit of the critical temperature in superconductivity to 310 K.

For the compound,the binary compound materials (TiFe, NbOs, Nb_3Al, NbC, MgRh, etc.[3]) are only used to determined definetly the atomic distance. There are no apparent correlation between T_c and **a**, because their relation should be given by some combination of the different elements which constitute the compound. But if we attend the abundance of the supercondactor with nearest interatomic distance, relative number of superconductor come to gather around 3, 4, 5 and 6 Å. In Fig.2 is plotted the number of superconductors and normal conductors [4] as a function of the nearest interatomic distance in crystal. As shown in Fig.2 there is a big differences between the distributions for the superconductive (a) and normal material (b) . It illustrates that there are some stable points in the atomic distance for the superconductor.

In the high temperature superconductor, it is considered that the CuO layer plays the fundamental role for a mechanism of superconductivity. So the critical temperature T_c is plotted as a function of the atomic distance **a** between Cu and O atoms, as shown in Fig.1. The data for high T_c superconductors, NdCeCuO, NdSrCeCuO, BaLaCuO, PbSrLaCuo, YBaCuO, BiCaSrCuO and TlCaBaCuO [1,5], are given in Table II. The data points lie close to the predicted lines in spite of a combination of different atoms. The critical temperature T_c become higher due to short atomic distances compared to the pure element superconductors.

In the fitting, there are some problems. For some elements (Be, W, etc.), the T_c are largely deviated from the predicted lines. It is neccessary to measure more precise value. As described above, the atomic orbits in the compound is bound with different states. Therefore it is neccessary to study the more detailed. Also for the high temperature superconducting material, we must study which atoms in the compound participate to the mechanism of superconductivity in more detailed.

To make progress in the understanding of high T_c superconductivity, we assume that the critical energy E_c, which is give by kT_c is proportional to the atomic overlap of the orbital electron density. We can obtain relations as follow. From the fitting, we can calculate the energy

$$E_c = kT_c = kT_0 \exp[-(6.87\mathbf{a})/(2v+1)],$$

where k is the Boltzmann constant and **a** is the atomic distance. In the calculation of the atomic electron orbits, the energy of resonance integral between atoms is given by the Pariser's equation [6]

$$E \sim \int(\phi^*\mathbf{H}\phi)dv \sim A \exp[-\mathbf{a}D],$$

where **H** is Hamiltonian of the electron, ϕ is the electron wave function, and **D** is a constant. If the quantum states of the electrons are considered, the constant **D** could be a function of some quantum number for the electron orbit. In the molecular orbital method, there is a relation that the overlap integral is propotional to the resonance integral [7]. Therefore, from the above point of view, the superconductivity may be connected

to electrons which play an important role in the overlap integral.

In conclusion, there is a discrete correlation in the relation between the superconducting critical temperature T_c and atomic distance **a** for pure element superconductors. These relations are represented by a simple equation;

$$T_c = 310 \exp(-aR_0/(2\nu+1)),$$

where R_0 = 6.87 and 5.53 $Å^{-1}$, and ν = 0, 1, 2, … . There are the other important results. (1) At the limit of **a** = 0, the upper limit of the critical temperature T_c is estimated at 310 K. (2) The elements(Li, Na, K, Rb, Cs ,Cu, Ag and Au) which belong to the group I in periodic table of the elements, have one s-state electron on the closed shells. If the s-state corresponds to ν= o, their critical temperature is estimated at ~ 10^{-5} K. (3) The isotope effect in the superconductivity could be caused by a change of the atomic distance. (4) The high T_c material could be produced by making the atomic distance short under the condition that the electrons are coherently bound in the same quantum electron orbits. (5) There are some stable points at the atomic distanc in a crystal for the superconductor.

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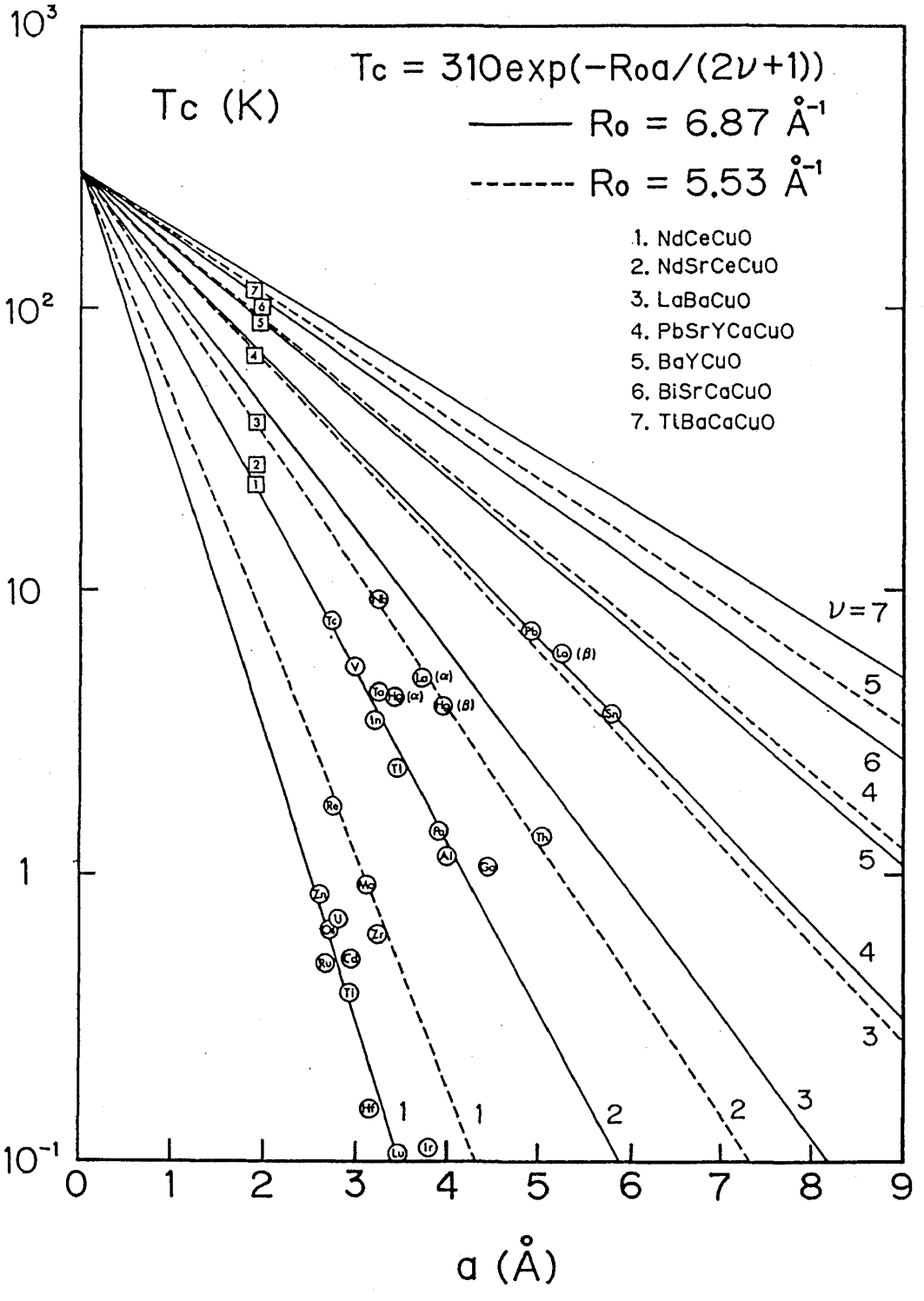
Table I. Critical temperature (T_c) and atomic distance (**a**) date of superconducting elements

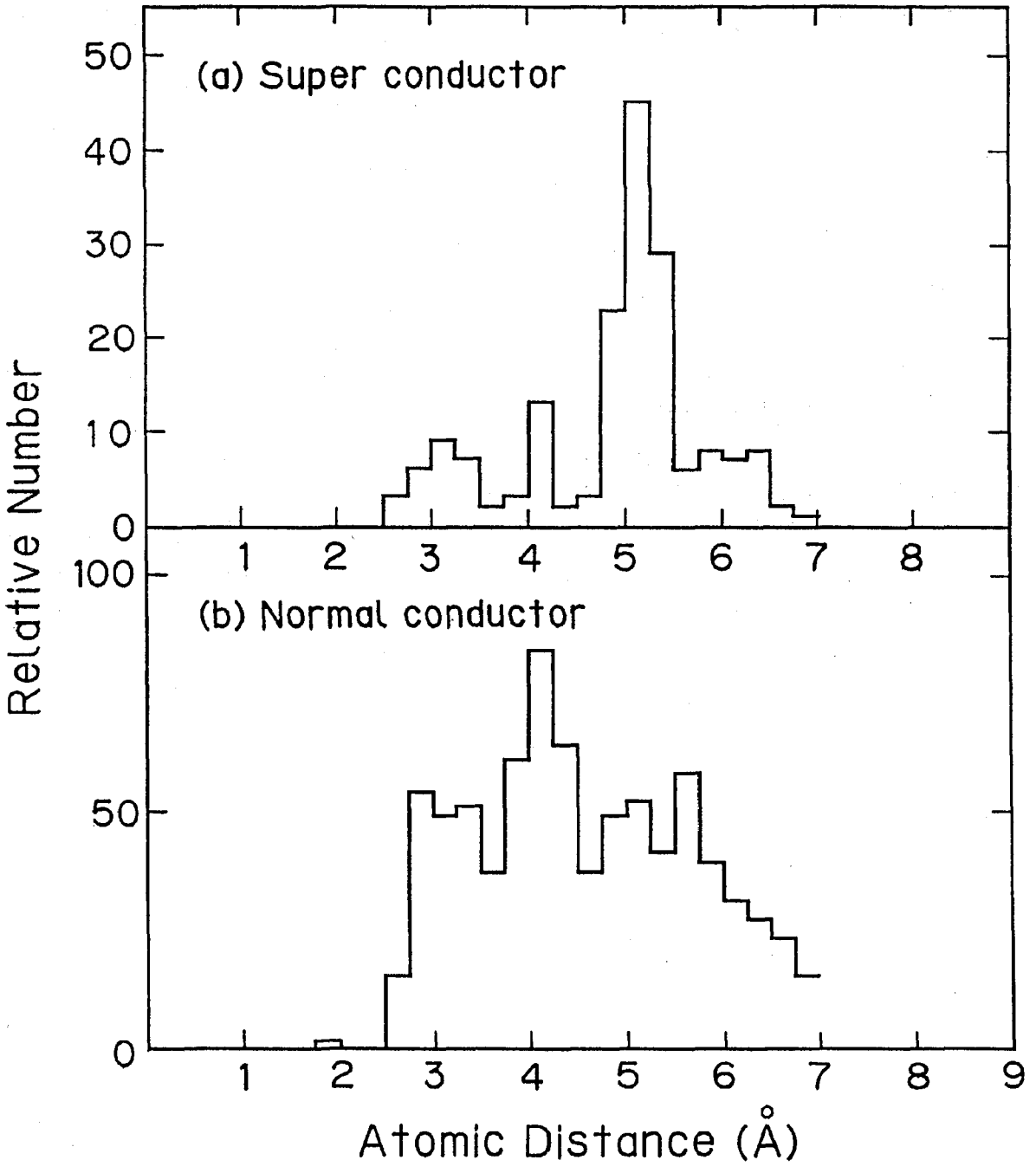
Element	Critical temperature T_c(K)	Atomic distance **a**(Å)	Structure type
Al	1.175	4.05	A1-Cu
Ir	0.1125	3.84	A1-Cu
β-La	6.00	5.30	A1-Cu
Pa	1.4	3.93	A1-Cu
Pb	7.196	4.95	A1-Cu
α-Th	1.38	5.08	A1-Cu
Mo	0.91	3.15	A2-W
Nb	9.25	3.30	A2-W
Ta	4.47	3.31	A2-W
V	5.40	3.04	A2-W
W	0.0154	3.17	A2-W
Be	0.026	2.29	A3-Mg
Cd	0.517	2.98	A3-Mg
Hf	0.128	3.20	A3-Mg
Lu	0.10	3.50	A3-Mg
Os	0.66	2.73	A3-Mg
Re	1.697	2.76	A3-Mg
Ru	0.49	2.70	A3-Mg
Tc	7.80	2.74	A3-Mg
Ti	0.40	2.95	A3-Mg
Tl	2.38	3.45	A3-Mg
Zn	0.85	2.66	A3-Mg
Zr	0.61	3.23	A3-Mg
α-La	4.88	3.77	A3'-La
β-Sn	3.722	5.83	A5-Sn
In	3.408	3.25	A6-In
α-Hg	4.154	3.46	A10-Hg
β-Hg	3.949	4.00	A10
Ga	1.083	4.52	A11-Ga
α-U	0.68-0.7	2.85	A20-U

Table II. Critical temperature (T_c) and Cu-O interdistance data of high T_c superconductors

Superconductor	Critical temperature (K)	Interdistance of Cu-O (Å)
BiSrCuO	22	(1.9)
NdCeCuO	24	1.93
NdSrCeCuO	28	1.92
LaBaCuO	30	1.89
PbSrYCaCuO	64	1.9
YBaCuO	91	1.94
BiAlCaCuO	114	1.95
BiSrCaCuO	105	1.92
TlCaBaCuO	120	1.92-1.99
BiCaSrCuO	120	(1.9)



1) The critical temperature T_c(K) versus atomic distance **a**(Å) in the elements [O] and the predicted lines that obtained by R_0 = 6.87 Å^{-1} (---) and 5.53 Å^{-1} (- - -). Also there are the data of high temperature superconductor [□].



2).The relative number of superconductor (a) and normal conductor (b) versus the nearest interatomic distance.